Polarized X-ray Fluorescence as a Probe of Ground State Properties

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Applicability of x-ray absorption sum rules to spectra detected with total fluorescence yield is studied by calculations in the ionic limit of the rare earth $3d \rightarrow 4f$ and transition metal $2p \rightarrow 3d$ spectra. We show that if no intermediate states with a high LS purity are reached, the dependence of the integrated intensity of fluorescence yield on the incoming polarization is mainly determined by the absorption step. Therefore, although in principle fluorescence yield is unequal to x-ray absorption, in the presence of a crystal field or of strong core-hole spin-orbit coupling fluorescence yield can be used to obtain ground state expectation values of L_z and S_z. [S0031-9007(96)00847-2]

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As a result of the rapid improvement in synchrotron technology x-ray magnetic dichroism (XMD) has become a useful probe in the study of magnetic materials [1–4]. Especially the development of sum rules [5,6] that relate the integrated intensity of the XMD spectra to ground state expectation values of various operators has increased the applicability of these techniques as tools for quantitative analysis of properties of magnetic materials. A variety of experimental techniques is used to measure the absorption intensity. Among them fluorescence yield (FY) has the great advantage over electron yield that it is less surface sensitive and that it has no magnetic field problems. Especially in the study of dilute systems, where self absorption effects play a minimal role, FY is increasingly used as a detection method.

Within the ionic limit the configurations of the main contribution to fluorescence are given by $|l^n\rangle \rightarrow |\underline{c}l^{n+1}\rangle \rightarrow |l^n\rangle$ where cl in this paper is $2p3d$ for transition metals and $3d4f$ for rare earths. Recently, doubts were raised from both experimental and theoretical sides [7–9] whether FY can provide information on ground state properties in a way similar to electron yield. This is questionable because of the significant variation in the fluorescence probabilities of the intermediate states as shown by de Groot *et al.* [9]. An example is given in Fig. 1 for a Dy^{3+} ion. One clearly observes a difference between the spectral line shapes for x-ray absorption (XAS) and fluorescence, resulting from a remarkable correlation between the polarization of the exciting light, the energy of the the intermediate states reached, and their fluorescence lifetimes. This paper shows that this variation of fluorescence lifetimes does not necessarily imply that FY is unsuitable for quantitative XMD analysis. We show this by an extensive study of polarized XAS and fluorescence on systems with spectra exhibiting strong multiplet effects.

The fluorescence decay step can be understood by considering the spectral vector $|v_q\rangle$,

$$|v_q\rangle = D_q^{(1)}|g\rangle = \sum_{\lambda\gamma\sigma}(-)^{l-\lambda}\begin{pmatrix} l & 1 & c \\ -\lambda & q & \gamma \end{pmatrix} l^\dagger_{\lambda\sigma}c_{\gamma\sigma}|g\rangle, \tag{1}$$

which is the vector reached after excitation of an electron from a core level c to the valence shell l by light q polarized along the magnetic axis. Factors such as reduced matrix elements that only lead to an overall scaling of the intensities have been omitted. Using the spectral vector we can easily express the integrated XAS intensity for q-polarized light, which is the sum of the squared matrix elements to all possible absorption final states $|n\rangle$,

$$I_q^{\mathrm{XAS}} = \sum_n \langle v_q|n\rangle\langle n|v_q\rangle = \langle v_q|v_q\rangle, \tag{2}$$

where removal of the final states by completeness gives the spectral weight as the squared norm of the spectral vector. These intensities obey the XAS sum rule [5],

$$\overline{I}^1 = \overline{I}_{q=1} - \overline{I}_{q=-1} = \frac{\langle L_z\rangle}{l\langle n_h\rangle}, \tag{3}$$

which relates the total integrated intensity of the circular dichroism spectrum $\overline{I}^1$ [10] to the ground state expectation value of the z component of the orbital momentum $\langle L_z\rangle$. ($\langle n_h\rangle$ is the number of holes. The intensities $\overline{I}^1$ are

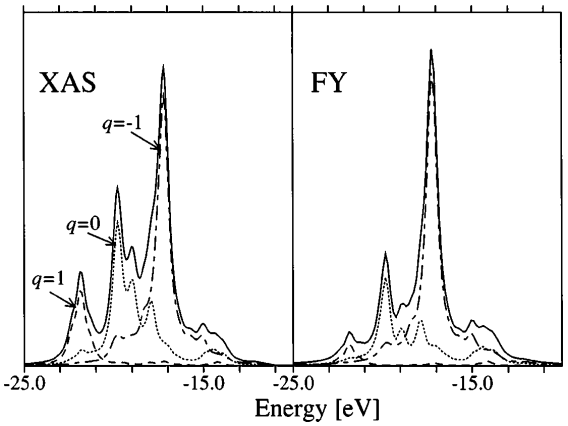

FIG. 1. Calculated spectra for the M_5 edge of a Dy^{3+} ion ($4f^9$). Left panel: XAS; right panel: fluorescence yield with isotropic detection. The solid lines show the spectra for incoming isotropic light. The contributions of the incoming polarization components are $q = 1$ (dashed), 0 (dotted), and -1 (dash-dotted). The absolute energy scale is arbitrary.

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normalized to the integrated intensity of the isotropic spectrum.)

We will now first show numerically that the information on $\langle L_z \rangle$ present in the x-ray absorption spectrum is still contained in the integrated intensities of the FY spectrum. We describe fluorescence as an x-ray inelastic scattering process (also known as x-ray emission spectroscopy),

$$J(\omega, \omega') = \frac{\Gamma}{\pi} \sum_f \left| \sum_n \frac{\langle f|D^{(1)}|n\rangle\langle n|D^{(1)}|g\rangle}{\omega + E_g - E_n + i\frac{\Gamma}{2}} \right|^2 \times \delta(E_g + \omega - E_f - \omega'). \quad (4)$$

By fluorescence we mean that an integration over the outgoing photon energy has been done. The total fluorescence yield also contains deexcitations by core levels, such as, e.g., $3s \rightarrow 2p$ for transition metals. It has been shown recently [11] that for isotropic outgoing light the sum rules for these processes are, up to a constant factor, equivalent to x-ray absorption. Hence they will only tend to increase the agreement between FY and absorption. Equation (4) has been calculated in the ionic limit using Cowan's programs [12]. For transition metals an octahedral crystal field ($10Dq = 1.0$ eV) has been applied. The intermediate state Auger lifetime broadening of the $c + \frac{1}{2}$ edge Γ has been taken 0.6 eV for rare earths and 0.4 eV for transition metals; we took twice these values for the $c - \frac{1}{2}$ edge.

The results for the normalized circular dichroism intensities of FY with isotropic detection [13] and of x-ray absorption are compared in Fig. 2. The fluorescence has been normalized with respect to the integrated intensity of the isotropic-in and isotropic-out spectrum. We find a good agreement between L_z values obtained by XAS (which are exact) and by fluorescence. For the average absolute error we find 0.12 for the rare earths (with $\langle L_z \rangle$ from 0.0 to 3.0) and 0.016 for transition metals (with $\langle L_z \rangle$ from -0.373 to 0.192). Especially for late transition metals the difference is small not only for the total integrated intensity $\overline{I}^1$, but also for the weighted difference of the integrated intensities of the two spin-orbit split edges $\overline{I}^1_{\rm diff}$ [14]. For XAS the latter value is equal to a linear combination of ground state expectation values of the spin-dependent operators S_z and T_z [6]. For $\overline{I}^1_{\rm diff}$ for late transition metals we find an average absolute error of 0.01 with $I_{\rm diff}$ from -0.46 to -0.10. Systematic differences occur for late rare earths. It is clear that the normalized integrated intensity of fluorescence is strongly related to that of XAS. In the remainder of the paper we establish the reason for this equality and the source of the deviations.

The major difficulty in analyzing $\overline{I}^1$ is the energy denominator of the intermediate states. As a result of the Auger lifetime broadening of the core hole Γ, intermediate states leading to the same final state can interfere. Two opposite approaches have been used. The incoherent approach [9] neglects all interference effects. This procedure clearly fails for systems where the energy spacing of the intermediate states is small relative to Γ. In this case the interference terms can contribute more than 50% to the total intensity.

On the opposite side, the fast collision approximation assumes that there is complete interference between all states within a spin-orbit split edge. This approach was successful in the interpretation of resonant (in)elastic scattering at the $2p \rightarrow 4f$ excitation edge of the rare earths [11,15]. Here the integrated intensity is related to ground state expectation values of two-particle operators. This approximation requires that the core-hole lifetime broadening Γ is larger than the energy spread of the spin-orbit split manifold. This condition is certainly not satisfied for the shallower core levels under consideration here.

The following analysis therefore explicitly takes into account the effect of a constant Auger lifetime broadening Γ. The integrated intensity for q-polarized incoming light is

$$I_q^{\rm fluor} = \sum_{\hat{\boldsymbol{\epsilon}}',n,n'} \langle \upsilon_q|n'\rangle\langle n'|V^\Gamma(\hat{\boldsymbol{\epsilon}}')|n\rangle\langle n|\upsilon_q\rangle. \quad (5)$$

The decay of the intermediate states is given by the "decay operator" $V^\Gamma(\hat{\boldsymbol{\epsilon}}')$. The decay for an arbitrary outgoing polarization vector $\hat{\boldsymbol{\epsilon}}'$ can be decomposed in terms of the standard unit polarization vectors with respect to the magnetic axis of our system, i.e., $V^\Gamma(\hat{\boldsymbol{\epsilon}}') = \sum_{qq'} \boldsymbol{\epsilon}'^*_{q'} \boldsymbol{\epsilon}'_q V^\Gamma_{q'q}$. After removal of the final states by completeness the matrix elements of $V^\Gamma_{q'q}$ are

$$\langle n'|V^\Gamma_{q'q}|n\rangle = g^\Gamma_{n'n} \sum_{\lambda\lambda'\gamma\gamma'\sigma\sigma'} \langle n'|l^\dagger_{\lambda'\sigma'} c_{\gamma'\sigma'} c^\dagger_{\gamma\sigma} l_{\lambda\sigma}|n\rangle \times (-)^{q'-\lambda'-\gamma} \begin{pmatrix} l & 1 & c \\ -\lambda' & -q' & \gamma' \end{pmatrix} \begin{pmatrix} c & 1 & l \\ -\gamma & q & \lambda \end{pmatrix}, \quad (6)$$

with $g^\Gamma_{n'n} = \Gamma^2/[(E_n - E_{n'})^2 + \Gamma^2]$. Diagonal terms give the probability of radiative decay of an intermediate state within the incoherent approximation. Off-diagonal terms are a result of interference between different intermediate states leading to the same final state. The latter matrix elements depend on Γ.

We can now obtain the most useful property of the decay operator by considering the matrix elements for the case of isotropic outgoing light. By commutation of the creation and annihilation operators we find that the matrix elements, and therefore the lifetimes of the intermediate states, are within a constant term equal to those of the $G^1_{\rm cl}$ exchange interaction,

$$\langle n'|V^\Gamma_{\rm iso}|n\rangle = \left\{ \frac{n_e + 1}{[l]}\,\delta_{n',n} - \frac{1}{[c](C^{l0}_{c0;10})^2} \sum_{\substack{\lambda\lambda'\gamma\gamma' \\ \sigma\sigma'}} \delta_{\gamma'-\lambda',\gamma-\lambda} c^1(c\gamma', l\lambda') c^1(c\gamma, l\lambda) \langle n'|c^\dagger_{\gamma\sigma} l^\dagger_{\lambda'\sigma'} l_{\lambda\sigma} c_{\gamma'\sigma'}|n\rangle \right\} g^\Gamma_{n'n}, \quad (7)$$

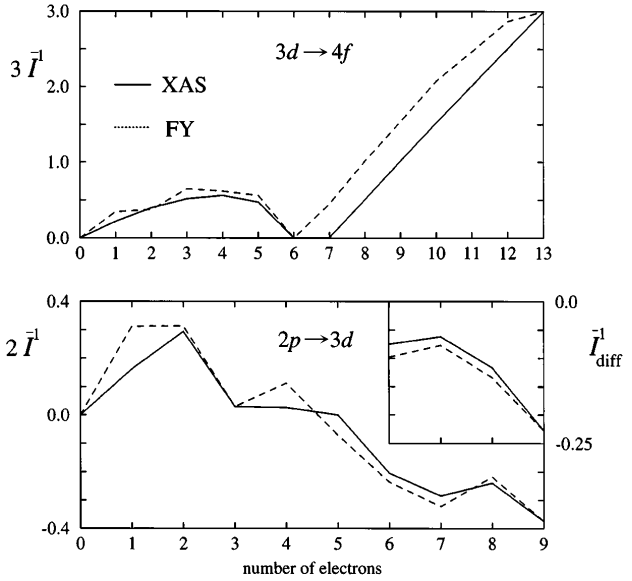

FIG. 2. Normalized integrated intensities of the circular dichroic fluorescence yield (dashed) and x-ray absorption (full) spectra of $3d$ and $4f$ ions. The y axis shows $l\bar{I}^1$ which for XAS is equal to $\langle L_z\rangle/\langle n_h\rangle$. The inset shows $\bar{I}^1_{\rm diff} = \bar{I}^1_{L_3} - 2\bar{I}^1_{L_2}$. For XAS on transition metals this is equal to $(\frac{2}{3}\langle S_z\rangle + \frac{7}{3}\langle T_z\rangle)/\langle n_h\rangle$.

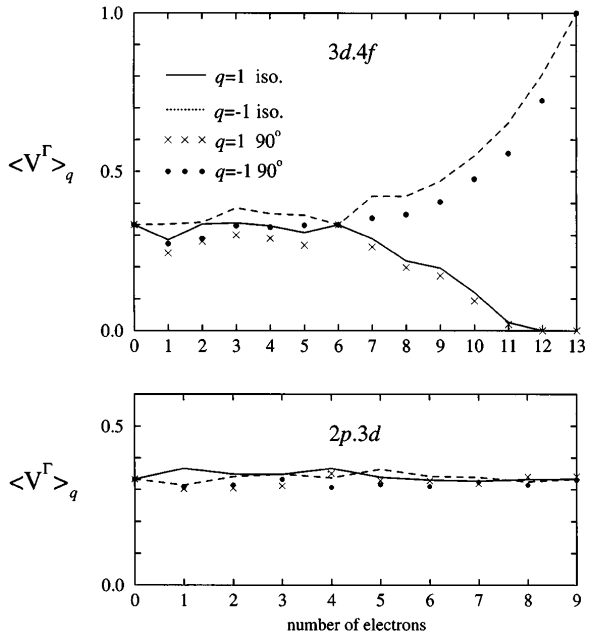

FIG. 3. The total decay $\langle V^\Gamma\rangle_q$ for the $4f$ (upper part) and $3d$ (lower part) series. The lines show the result for a measurement with outgoing isotropic light [$q = 1$ (solid), -1 (dashed)]. The symbols correspond to a measurement with the detector at 90° [$q = 1$ (crosses), -1 (dots)].

where $[j] = 2j + 1$, $n_e + 1$ is the number of electrons in the intermediate state, and $c^k(c\gamma, l\lambda)$ are the Slater-Condon parameters [16]. The exchange Coulomb term $G^1_{\rm cl}$ is for a large part responsible for the relative position of the intermediate states within a spin-orbit split manifold. This immediately explains why the states at the low energy side of the edge have on average a smaller decay probability than those on the high energy side, see, e.g., Fig. 1.

We can also directly compare the integrated intensity of the fluorescence to that of x-ray absorption by changing from the eigenvector basis $|n\rangle$ to a basis set that contains the normalized spectral vector, $|\overline{v}_q\rangle = |v_q\rangle/\sqrt{\langle v_q|v_q\rangle}$.

$$\begin{aligned} I^{\rm fluor}_q &= \sum_{\hat{\boldsymbol{\epsilon}}'}\langle v_q|\overline{v}_q\rangle\langle\overline{v}_q|V^\Gamma(\hat{\boldsymbol{\epsilon}}')|\overline{v}_q\rangle\langle\overline{v}_q|v_q\rangle \\ &= \langle v_q|v_q\rangle\sum_{\hat{\boldsymbol{\epsilon}}'}\langle\overline{v}_q|V^\Gamma(\hat{\boldsymbol{\epsilon}}')|\overline{v}_q\rangle \\ &= I^{\rm XAS}_q\langle V^\Gamma\rangle_q. \end{aligned} \tag{8}$$

Expressing the fluorescence intensity in this way clearly shows that a constant decay for *all* the intermediate states is not a necessary requirement for the use of fluorescence as a tool for quantitative XMD analysis; the only requirement is that the *total* decay $\langle V^\Gamma\rangle_q$ must not have a strong polarization dependence.

Figure 3 shows the values of $\langle V^\Gamma\rangle_q$ for measurements both with the outgoing light detected isotropically [13] as well as with the detector at $\theta = 90°$ to the magnetic axis. For clarity the values for $q = 0$ have been omitted; they can be obtained from the normalization $\sum_q\langle V^\Gamma\rangle_q = 1$. When $\langle V^\Gamma\rangle_q = \frac{1}{3}$ for all q, there is no polarization dependence of the total decay. Figure 3 shows that only for late rare earths are significant deviations from this value found.

This can be understood when we realize that for a strong polarization dependence of the total decay $\langle V^\Gamma\rangle_q$ two conditions have to be satisfied. First, since the decay is proportional to a Coulomb interaction there have to be groups of states of pure LS character resulting in strongly different values for $G^1_{\rm cl}$. On the other hand, states which, due to spin-orbit interaction, are a mixture of LS terms do not lead to extreme values for $\langle V^\Gamma\rangle_q$. States with maximum values of LSJ, which occur only in the $j = c + \frac{1}{2}$ edge, have pure LS character because they are the only states for that J.

Second, the symmetry of the ground state has to be such that the intermediate states with high LS purity can be preferably reached for some polarization. This is not so for ions early in the series, where the states with maximum LSJ are spin forbidden. Furthermore, when a crystal field produces a ground state which has no pure LS character, any preference for specific intermediate state LS terms disappears.

These two criteria are certainly present in the late rare earths. They have a Hund's rule ground state, and high LSJ intermediate states can be reached. In the simple case of Tm^{3+}, e.g., the absorption for $q = 1$ is zero, and the only decay ratio of interest is $\langle V^\Gamma\rangle_{-1}/\langle V^\Gamma\rangle_0 = 4.2$. The normalized spectral vectors starting from a $4f^{12}(^3H_6; M_J = 6)$ ground state

are $|\overline{v}_0\rangle = |\underline{3d}4f^{13}(^3H_6)\rangle$ and $|\overline{v}_{-1}\rangle = |\underline{3d}4f^{13}(^3G_5)\rangle$. A good estimate of the fluorescence decay ratio for $q = -1$ and $q = 0$ is obtained by evaluating Eq. (7) with $g_{n'n}^{\Gamma=\infty} = 1$. A straightforward calculation [16] gives $[5]\langle\overline{v}_{-1}|V_{\rm iso}^{\Gamma=\infty}|\overline{v}_{-1}\rangle/[6]\langle\overline{v}_0|V_{\rm iso}^{\Gamma=\infty}|\overline{v}_0\rangle = 4.4$ (the factor $[J]$ accounts for the multiplicity of the levels).

This dependence of the decay causes a variation of the yield with detection angle. For q-polarized ingoing light the total fluorescence intensity,

$$I_q^{\rm fluor}(\cos\theta) = \tfrac{2}{3}I_q^{z'=0} + \tfrac{1}{3}(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})I_q^{z'=2}, \quad (9)$$

is an angle dependent combination of the intensities for isotropic outgoing light ($z' = 0$) and linear dichroic outgoing light ($z' = 2$). (Combinations z' of the outgoing polarization q' are defined according to Ref. [10].) So for measurement in a 90° configuration the intensity for q-polarized ingoing light is given by $I_{q0} + \frac{1}{2}\{I_{q1} + I_{q-1}\}$, and we see that changing the detection angle causes a preference for a certain decay channel, here $q' = 0$. In cylindrical symmetry the dominant contribution to the fluorescence spectrum (the elastic part) comes from $q' = -q$, and thus, compared to isotropic outgoing light, we find an increased fluorescence yield for linearly polarized light ($q' = 0$) with respect to that for circularly polarized light ($q' = \pm 1$). The ratio between the left and right polarized decay channels changes little.

If the valence shell were only a spectator in the decay process [as is the case in resonant Raman spectroscopy [11] ($l^n \rightarrow \underline{c}_1 l^{n+1} \rightarrow \underline{c}_2 l^{n+1}$) and certain resonant photoemission processes [17] ($l^n \rightarrow \underline{c}_1 l^{n+1} \rightarrow \underline{c}_2^2 l^{n+1}$)], the ($z' = 0$) and ($z' = 2$) contributions have been shown to measure the monopole and the quadrupole of the core hole created in the absorption process. However, because the valence shell is involved in the decay and V^Γ depends on the intermediate states, an interpretation of the angular dependence of fluorescence is complicated. Further investigation is also necessary to clarify the information contained in fluorescence on valence band excitations, such as, e.g., magnons and plasmons.

In conclusion, we have studied the relation between the total integrated intensities of x-ray absorption and fluorescence. Despite the fact that the fluorescence lifetimes of the intermediate states vary strongly, the polarization dependence of the integrated fluorescence intensities is mainly determined by the absorption step in the situations where no intermediate states with high LS purity are reached. In the presence of a crystal field or of strong mixing by core-hole spin-orbit coupling polarization effects due to the decay are small. Information on ground state expectation values of L_z and S_z can therefore also be obtained by fluorescence yield detection.

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$$\overline{I}^z = \sum_q (-)^{1-q} \begin{pmatrix} 1 & z & 1 \\ -q & 0 & q \end{pmatrix} \begin{pmatrix} 1 & z & 1 \\ -1 & 0 & 1 \end{pmatrix}^{-1} \overline{I}_q \, .$$

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